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白粉藤的木脂素和三萜成分

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摘要：从白粉藤 (*Cissus repens* Lank) 地上部分分离得到5个木脂素和8个三萜，其中一个木脂素是新化合物，它的结构通过波谱分析和碱水解的方法鉴定为：(+)-异落叶松树脂醇-9′-(2-对-香豆酰)-*O*-β-*D*-吡喃木糖苷 (1)。其余化合物分别是：(+)-异落叶松树脂醇-9′-*O*-β-*D*-吡喃木糖苷 (2)，(+)-Lyoniside (3)，(—)-开环异落叶松树脂醇-9-*O*-β-*D*-吡喃木糖苷 (4)，(7′*R*, 8′*S*)-4′-hydroxy-3′, 5-dimethoxy-7′, 8′-dihydrobenzofuran-1-propanolneolignan-9′-*O*-β-*D*-xylopyranoside (5)，木栓酮 (6)，表木栓醇 (7)，蒲公英赛醇乙酸酯 (8)，熊果酸 (9)，2α-羟基乌索酸 (10)，积雪草酸 (11)，Niga-ichigoside F1 (12)，羽扇豆醇 (13)。这些化合物都是首次从该植物中分离得到。

关键词：白粉藤；葡萄科；木脂素；五环三萜
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Lignans and Triterpenoids from *Cissus repens* (Vitaceae)*

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Abstracts: Five lignans and eight triterpenoids were isolated from the aerial parts of *Cissus repens*. Among them, a lignan, (+)-isolariciresinol-9′-(2-*p*-coumaric)-*O*-β-*D*-xylopyranoside (1), was new and its structure was established on the basis of spectroscopic methods and alkaline hydrolysis. Other compounds, (+)-isolariciresinol-9′-*O*-β-*D*-xylopyranoside (2), (+)-lyoniside (3), (—)-secoisolariciresinol-9-*O*-β-*D*-xylopyranoside (4), (7′*R*, 8′*S*)-4′-hydroxy-3′, 5-dimethoxy-7′, 8′-dihydrobenzofuran-1-propanolneolignan-9′-*O*-β-*D*-xylopyranoside (5), friedelin (6), epifriedelanol (7), taraxerol-3β-acetate (8), ursolic acid (9), 2α-hydroxyursolic acid (10), asiatic acid (11), niga-ichigoside F1 (12) and lupeol (13), were found in the plant for the first time.

Key words: *Cissus repens*; Vitaceae; Lignans; Pentacyclic triterpenoids

Cissus repens Lamk., a climber, belongs to the family Vitaceae and distributes in Southern China and Taiwan, Guizhou and Yunnan Province. The roots and stems of *C. repens* were used for treatment of snake bites, rheumatic pains and carbuncles in Chinese folk, and the latter were also employed to treat nephritis,

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long-term cough and diarrhea (China National Bureau of Chinese Traditional Medicine, 1999). The components of the plant remain unknown as yet. In the present research, five lignans (1-5) and eight triterpenoids (6-13) were isolated from the aerial parts of the plant. Among them, a lignan, (+)-isolariciresinol-9′-(2-*p*-coumaric)-*O*-β-*D*-xylopyranoside (1), was new. This paper reports the structural elucidation of the new compound. In addition, the ^{13}C NMR data of 4 were assigned for the first time. Compound 1 was obtained as a white amorphous powder and its molecular formula was deduced as $C_{34}H_{38}O_{12}$ by the $[M-H]^-$ ion peak at *m z* 637.2280 (calc. 637.2285) in the HRESIMS. The IR spectrum of 1 showed absorption bands for hydroxyl group (ν_{max} 3451 cm^{-1}), conjugated carbonyl (ν_{max} 1712 and 1632 cm^{-1}) and phenyl ring (ν_{max} 1606 and 1515 cm^{-1}). In the ^{1}H- and ^{13}C-NMR spectra of 1, the signals at δ_H 7.40 (d, *J* = 8.5 Hz, 2H, H-2 and H-6) and 6.77 (d, *J* = 8.5 Hz, 2H, H-3 and H-5), and δ_C 131.0 (d, C-2 and C-6) and 116.7 (d, C-3 and C-5) were owing to the existence of a 4-hydroxyphenyl group. The signals at δ 7.60 (d, *J* = 15.9 Hz, 1H, H-7) and 6.39 (d, *J* = 15.9 Hz, 1H, H-8) showed the presence of a *trans* olefin bond in 1. There was a (+) or (—)-isolariciresinol-9′-*O*-β-*D*-xylopyranoside moiety in 1 by comparison of the ^{1}H and ^{13}C NMR data of 1 with those in the literatures (Zuo *et al*, 2005; Zhang *et al*, 1999). The remained moiety contained a carbonyl, a *trans* olefin bond and a 4-hydroxyphenyl group, which indicated that 1 bore a *p*-coumaric group. The linkage of the *p*-coumaric substi-

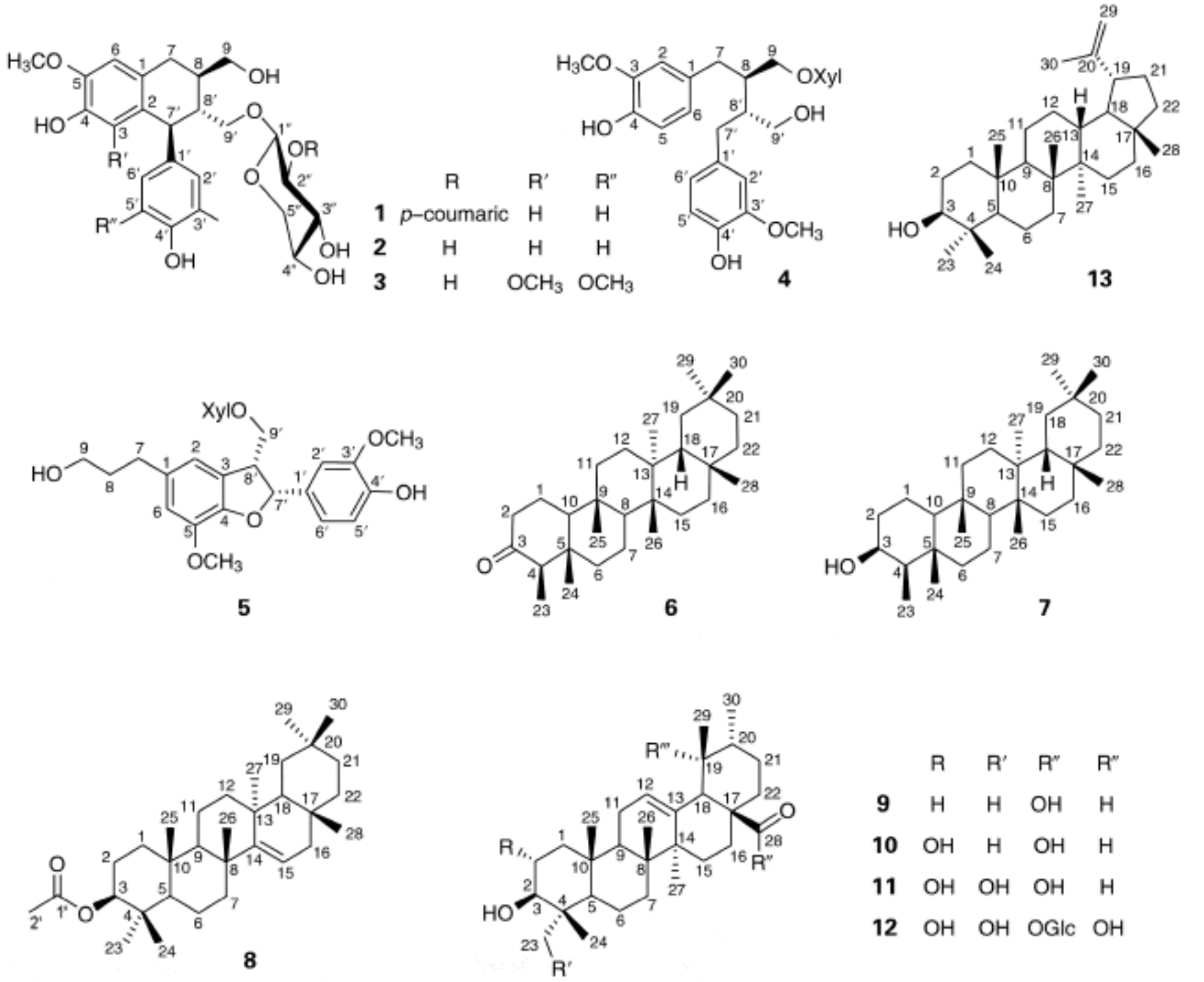

Fig. 1 Structures of compounds 1-13

tuent to 2″-OH was established by the HMBC spectrum, in which H-2″ was correlated to the ester carbonyl carbon (δ_C 167.4, C-9′). After basic hydrolysis of 1, (+)-isolariciresinol-9′-*O*-β-*D*-xylopyranoside was harvested and confirmed by TLC comparing with authentic samples and optical rotation ($[\alpha]_D^{19}$). Thus, the structure of 1 was elucidated as (+)-isolariciresinol-9′-(2-*p*-coumaric)-*O*-β-*D*-xylopyranoside.

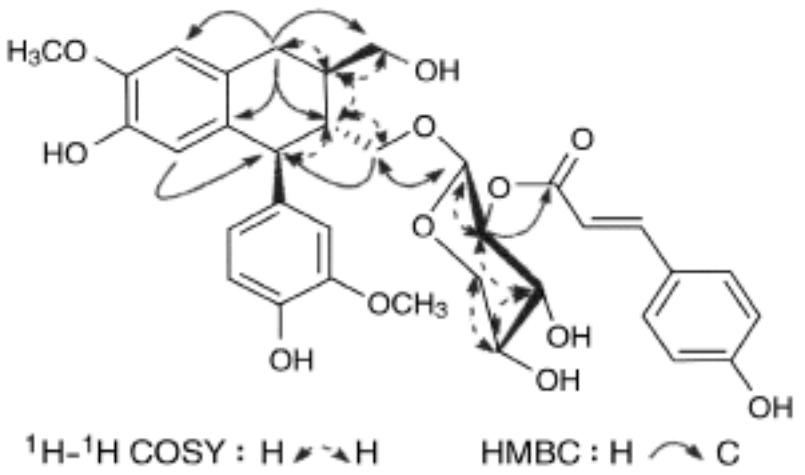

Fig. 2 Key ^{1}H-^{1}H COSY (bold) and HMBC (arrow) correlations for 1

Experimental

General Experimental Procedures Column chromatography was performed over silica gel (200-300 and 300-400 mesh), silica gel H (10-40 μm; Qingdao Marine Chemical Ltd., Qingdao, P. R. China) and Sephadex LH-20 (40-70 μm; Amersham Pharmacia Biotech AB, Uppsala, Sweden). TLC was performed on precoated plates with silica gel F_{254} (Qingdao). 1D and 2D spectra were recorded on BRUKER AM-400 and DRX-500 spectrometers. MS were measured on a VG Auto Spec-3000 mass spectrometer. Optical rotations were determined on a JASCO DIP370 digital polarimeter. IR spectra were recorded on a Bio-Rad FTS-135 infrared spectrophotometer. The UV spectrum was recorded on a Shimadzu double-beam 210A spectrometer.

Plant Material The aerial parts of *C. repens* were collected from Xishuangbanna, Yunnan Province of P. R. China, in August 2004. The plant was identified by professor De-Ding Tao (Kunming Institute of Botany, Chinese Academy of Sciences), and a voucher specimen was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation The aerial parts of *C. repens* (3.0 kg) were extracted thrice with EtOH (95%). The solvent was evaporated to give a residue, which was suspended in water and participated with petrol, EtOAc and n-BuOH successively. The EtOAc extract (23.8 g) was fractionated by silica gel column chromatography ($CHCl_3$-MeOH, 10∶1, 5∶1 and 3∶1) to afford four major fractions (I-IV).

Fraction I was purified by repeat silica gel column chromatography ($CHCl_3$; petrol-EtOAc, 50∶1; petrol-acetone, 30∶1) to give 6 (161 mg), 7 (86 mg), 8 (5 mg) and 13 (77 mg). Fraction II was purified by repeated silica gel column chromatography ($CHCl_3$-acetone, 3∶1-1∶1; $CHCl_3$-MeOH, 20∶1-10∶1) to give 9 (14 mg), 10 (23 mg) and 11 (20 mg). Fraction III was purified by RP-18 (MeOH-H_2O, 50∶50) and silica gel ($CHCl_3$-acetone, 1∶2; EtOAc-acetone, 1∶2) column chromatography to afford 1 (136 mg), 2 (22 mg) and 5 (8 mg). Fraction IV was purified by repeated silica gel ($CHCl_3$-MeOH, 8∶1-3∶1; $CHCl_3$-acetone, 1∶5) and Sephadex LH-20 (MeOH) column chromatography to yield 3 (30 mg), 4 (5 mg) and 12 (13 mg).

(+)-Isolariciresinol-9′-(2-*p*-coumaric)-*O*-β-*D*-xylopyranoside (1). $C_{34}H_{38}O_{12}$, white amorphous powder (MeOH); $[\alpha]_D^{23}$ -13.5° (MeOH, *c* 0.52); UV λ_{max}^{MeOH} (log ε): 315.2 (4.28), 290.2 (4.26) nm; IR ν_{max}^{KBr} cm^{-1}: 3451, 1712, 1632, 1606, 1515, 1272, 1178, 1081, 1029; FABMS: *m z* 637 [M-H]$^-$; HRESIMS *m z* 637.2280 [M-H]$^-$ (calcd. for $C_{34}H_{37}O_{12}$: 637.2285); ^{1}H and ^{13}C NMR data see Table 1.

Table 1 ^{1}H and ^{13}C NMR data of compound 1 (δ ppm, *J* Hz)[a]

atom	δ_H	δ_C	atom	δ_H	δ_C	atom	δ_H	δ_C
1		128.6s	3′		148.7s	5″	3.80(m,1H), 3.15 (m,1H)	66.7t
2		133.9s	4′		146.0s	1		126.9s
3	5.98 (s, 1H)	117.0d	5′	6.63 (d, 8.0, 1H)	113.6d	2,6	7.40 (d, 8.5, 2H)	131.0d
4		145.2s	6′	6.53 (d, 8.0, 1H)	123.3d	3,5	6.77 (d, 8.5, 2H)	116.7d
5		146.7s	7′	3.79 (m, 1H)	47.5d	4		160.9s
6	6.54 (s, 1H)	112.2d	8′	1.79 (m, 1H)	45.2d	7	7.60 (d, 15.9, 1H)	146.4d
7	2.73 (m,1H),2.72 (m,1H)	33.5t	9′	3.82(m,1H), 3.11 (m,1H)	68.7t	8	6.39 (d, 15.9, 1H)	115.5d
8	1.94 (m, 1H)	38.8d	1″	4.29 (d, 8.0, 1H)	103.5d	9		167.4s
9	3.60 (m, 2H)	64.7t	2″	4.78 (t, 8.0, 1H)	75.0d	-OMe	3.68 (s, 3H)	56.2q
1′		133.9s	3″	3.53 (m, 1H)	75.9d	-OMe	3.71 (s, 3H)	56.4q
2′	6.57 (d, 1.3, 1H)	115.8d	4″	3.54 (m, 1H)	71.2d			

a: NMR data of 1 measured in CD_3OD at 500 MHz for proton and 125 MHz for carbon.

(+)-Isolariciresinol-9′-*O*-β-*D*-xylopyranoside (2). $C_{25}H_{32}O_{10}$, white amorphous powder ($CHCl_3$-MeOH); ESIMS *m z* 491 [M-H]$^-$; ^{13}C NMR data: same as the data reported in Zou *et al* (2005).

(+)-Lyoniside (3). $C_{27}H_{36}O_{12}$, white amorphous powder (MeOH); $[\alpha]_D^{25}$ +9.0° (MeOH, *c* 0.45); ESIMS *m z* 551 [M-H]$^-$; ^{13}C NMR data: same as the data reported in Inoshiri *et al* (1987).

(—)-secoisolariciresinol-9-*O*-β-*D*-xylopyranoside (4). $C_{25}H_{34}O_{10}$, colourless amorphous solid (MeOH); $[\alpha]_D^{19}$ -25.0° (MeOH, *c* 0.60); ESIMS *m z* 493 [M-H]$^-$; ^{13}C NMR data (400 MHz, CD_3OD) δ_C 148.8 (s, C-3 and C-3′), 145.5 (s, C-4 and C-4′), 134.0 (s, C-1′), 133.9 (s, C-1), 122.8 (d, C-6 and C-6′), 115.8 (d, C-5 and C-5′), 113.6 (d, C-2′), 113.5 (d, C-2), 105.2 (d, C-1″), 78.0 (d, C-3″), 75.0 (d, C-2″), 71.3 (d, C-4″), 70.2 (t, C-9), 67.0 (t, C-5″), 62.8 (t, C-9′), 56.9 (q, -OMe×2), 44.4 (d, C-8′), 41.7 (d, C-8), 35.7 (t, C-7′), 35.6 (t, C-7); The data of optical rotation and ^{1}H NMR are similar to those data reported in Lundgren *et al* (1985).

(7′*R*, 8′*S*)-4′-Hydroxy-3′, 5-dimethoxy-7′, 8′-dihydrobenzofuran-1-propanolneolignan-9′-*O*-β-*D*-xylopyranoside (5). $C_{25}H_{32}O_{10}$, colourless solid (acetone); FABMS *m z* 491 [M-H]$^-$; ^{13}C NMR data: same as the data repoted in Kouno *et al* (1993).

Friedelin (6). $C_{30}H_{50}O$, colourless needles ($CHCl_3$); EIMS *m z* [M]$^+$ 426 (52%), 411 (12), 341 (7), 302 (25), 273 (100), 95 (83), 123 (93), 69 (81); ^{13}C NMR data: same as the data reported in Klass *et al* (1992).

Epifriedelanol (7). $C_{30}H_{52}O$, colourless flakes ($CHCl_3$); EIMS *m z* [M]$^+$ 428 (28%), 413 (29), 275 (90), 125 (92), 95 (100), 69 (84); ^{13}C NMR data: same as the data reported in Kundu *et al* (2000).

Taraxerol-3β-acetate (8). $C_{32}H_{52}O_2$, colourless needles ($CHCl_3$); EIMS *m z* [M]$^+$ 468 (14%), 453 (10), 344 (50), 204 (100); ^{13}C NMR data: same as the data reported in Li *et al* (1998).

Ursolic acid (9). $C_{30}H_{48}O_3$, white amorphous powder ($CHCl_3$-MeOH); ^{13}C NMR data: same as the data reported in Yang and Zhao (2003).

2α-Hydroxyursolic acid (10). $C_{30}H_{48}O_4$, white amorphous powder ($CHCl_3$-MeOH); FABMS *m z* 471 [M-H]$^-$; ^{13}C NMR data: same as the data reported in Gao *et al* (2004).

Asiatic acid (11). $C_{30}H_{48}O_5$, white amorphous powder (MeOH); FABMS *m z* 487 [M-H]$^-$; ^{13}C NMR data: same as the data reported in Zhang *et al* (1997).

Niga-ichigoside F1 (12). $C_{36}H_{58}O_{11}$, colourless needles (MeOH); FABMS *m z* 665 [M-H]$^-$; ^{13}C NMR data: same as the data reported in Seto *et al* (1984).

Lupeol (13). Colourless needles (petrol-EtOAc); determined by TLC with the authentic sample.

Weak alkaline hydrolysis of 1. Nine milligrams of 1 were dissolved in 20 ml solution (MeOH-H_2O, 1∶1) containing appropriate Na_2CO_3 and hydrolyzed under reflux (2 h) at 45℃. Then, the basic solution was evaporated in vacuo to dryness and separated by silica gel column chromatography eluted with $CHCl_3$-MeOH (10∶1) to yield 6 mg of (+)-isolariciresinol-9′-*O*-β-*D*-xylopyranoside detected by TLC and optical rotation, $[\alpha]_D^{19}$ +40.6° (pyridine; *c* 0.60).

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